

Fourth Annual Conference on Carbon Capture & Sequestration

*Developing Potential Paths Forward Based on the
Knowledge, Science and Experience to Date*

Geologic Sequestration (3)

Effective Use of Brines for CO₂ Sequestration

Gillian M. Bond

May 2-5, 2005, Hilton Alexandria Mark Center, Alexandria Virginia



Authors

- New Mexico Tech:
Gillian M. Bond
Shingo Date
Ning Liu
Teri Dunn
Thomas Villanova
Christa Hockensmith
Brian J. McPherson
- EPRI/Izambard:
John Stringer

Natural sequestration in carbonates

- Generation of carbonates by marine organisms, as in formation of oolithic limestone beds
 - Process requires removal of product from ocean for permanent sequestration
 - Achieved by sedimentation and geological shifts (e.g. the Permian Basin)
- Weathering reactions leading to carbonation of silicates
- Can we mimic these processes?

From CO_2 to calcium carbonate

- If concentrations of Ca^{2+} and CO_3^{2-} ions in aqueous solution exceed the solubility limit
 - CaCO_3 can be precipitated
- The issue for CO_2 fixation
 - how to get from CO_2 to CO_3^{2-} quickly
 - bicarbonate must be formed first

Biomimetic sequestration

- Hydration of CO_2 is rate-limiting step in reaction sequence
- CO_2 fixation as carbonate is potentially viable if we can speed up this reaction
- Hydration of CO_2 accelerated by an enzyme or biological catalyst
 - Carbonic anhydrase

Cation sources for carbonate formation

- Sources will be location specific
- Possible sources include:
 - Seawater
 - Brines, including:
 - produced waters from oil and gas production
 - waste streams from various industrial processes
 - waste brines from desalination
- Use of waste streams offers possibility of adding value to an existing waste product

Produced waters

- Cation concentrations and total dissolved solids (TDS) vary from reservoir to reservoir
- Some usage in water flooding for postsecondary production
- Mostly a waste product
- ~ 90 % reinjected for disposal in Permian Basin
 - moved by truck or pipeline
- Addition of value to this waste product would be attractive

Summary of earlier results

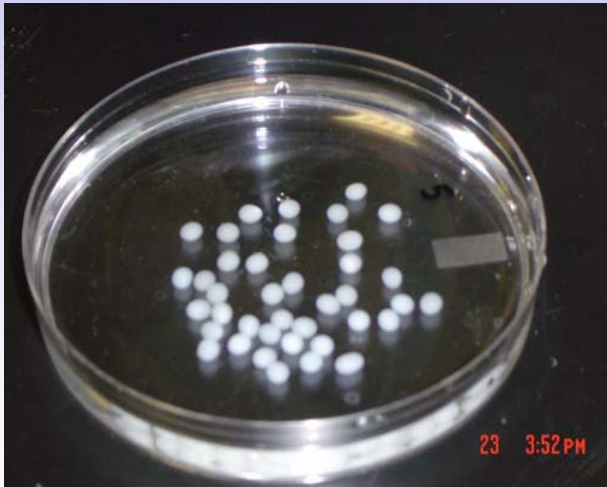
- Viability of produced waters as cation source demonstrated at both bench and laboratory scale
- Sequestration rate and efficiency in pH range ~ 8.5 influenced by:
 - Carbonic anhydrase
 - Total inorganic carbon (IC)
 - Calcium ion concentration
 - Ratio of Ca^{2+} : Mg^{2+} concentrations
 - Decrease in supersaturation on precipitation
 - Temperature

Present goals

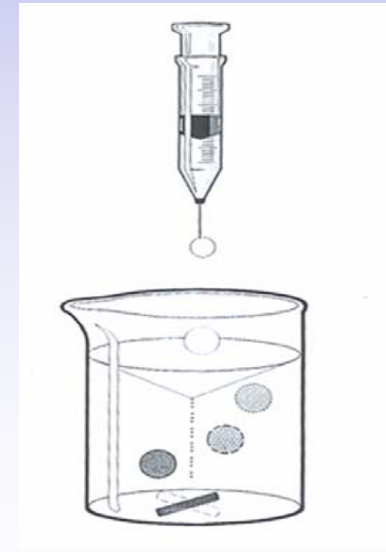
- To observe system performance over longer laboratory-scale runs
- To perform experiments with CO₂-saturated brine (rather than CO₂-saturated DI water plus brine)
 - more closely simulates industrial application
 - gives higher supersaturation
- To investigate the efficacy of brine recycling for brines with high Ca²⁺ content
 - precipitation during early cycles is limited by IC depletion

Immobilization of enzyme in beads

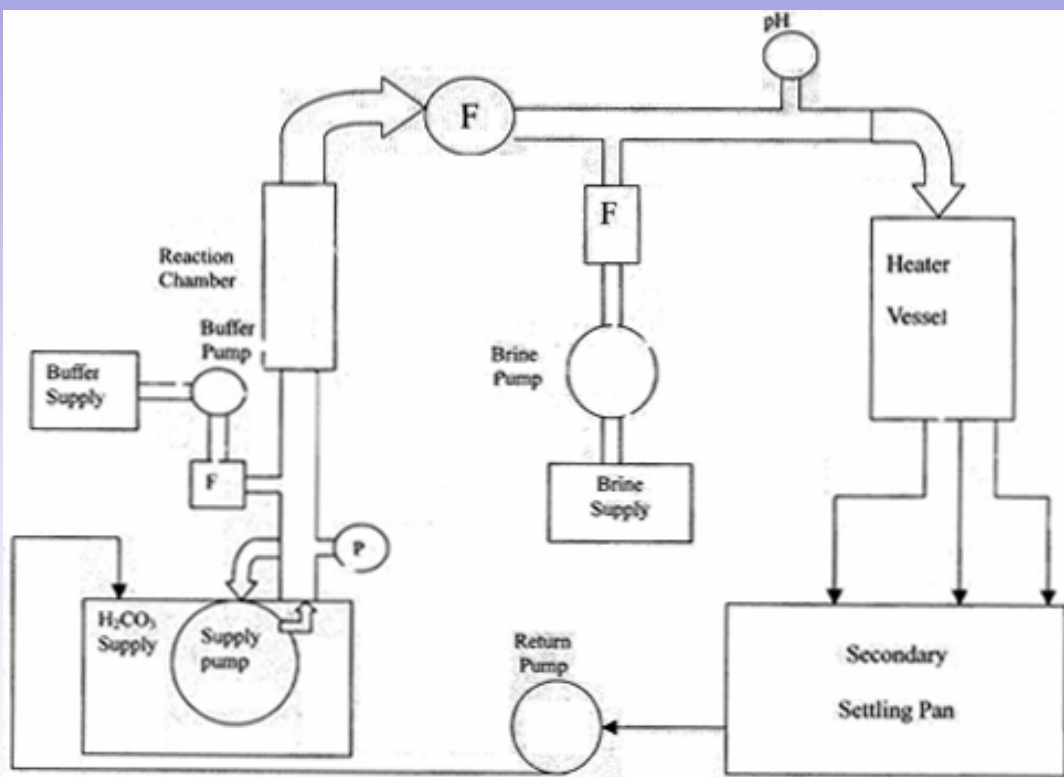
0.1 mg/ml of bovine carbonic anhydrase (BCA) dissolved in 2% w/v alginic acid in DI water. Drops of this solution added to 0.2M CaCl_2 solution (crosslinking agent) with 2% w/v chitosan



Picture of the prepared beads



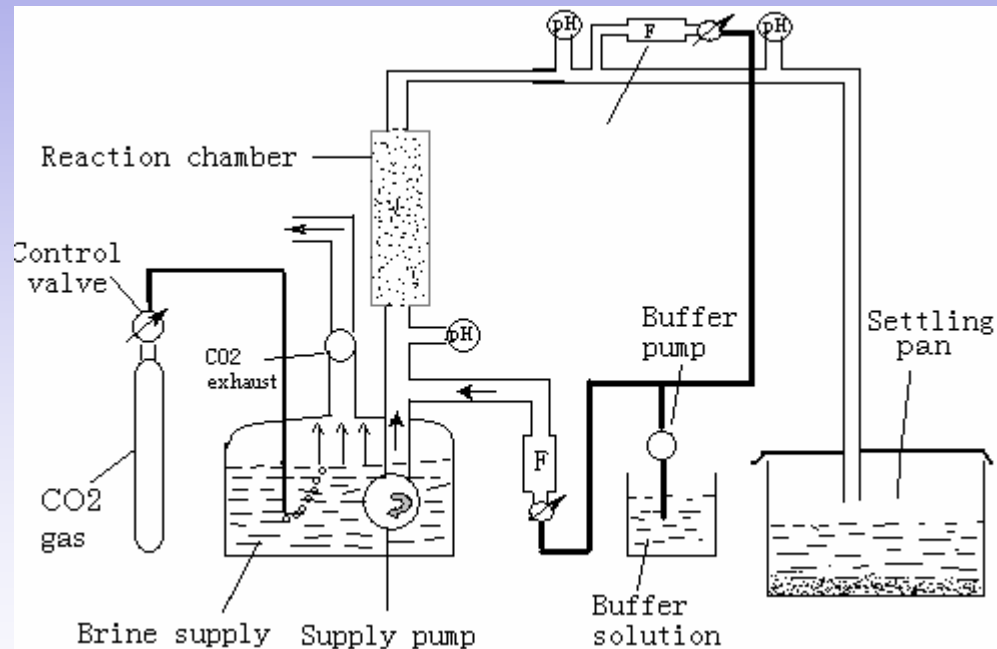
Laboratory scale reactor system



Laboratory-scale experiments

- Selection of flow rates for initial experiments in laboratory-scale reactor system
 - Inflow rate of CO₂-saturated solution ~1.1 l/min
 - Inflow rate of produced water ~1.0 l/min
 - Inflow rate of 1M Tris buffer solution 0.15 l/min

Apparatus for experiments with CO_2 -saturated brine



Product analyses

Concentrations of calcium ions and IC in produced waters

- IC Shimadzu TOC-5050A
- Ca^{2+} ions Varian SpectrAA 220 and Instrumental Laboratory Video 12 aa/ae spectrophotometer

Precipitates

- Powder XRD Siemens D500
- SEM observation JEOL JSM-6100 SEM

Compositions of high-TDS produced water from Permian and San Juan Basins

mol/l	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS [ppm]	Ca ²⁺ : Mg ²⁺
Permian Basin ¹	2.69	8.72x10 ⁻²	1.47x10 ⁻¹	4.62x10 ⁻³	3.06	2.10x10 ⁻²	2.20x10 ⁻³	1.80x10 ⁵	1 : 1.7
San Juan Basin ²	1.34	1.74x10 ⁻¹	6.92x10 ⁻²	5.23x10 ⁻³	1.80	1.11x10 ⁻²	2.80x10 ⁻³	1.05x10 ⁵	2.5 : 1

¹ J. Krumhansl, R. Pawar, *et al.* "Geologic Sequestration of Carbon Dioxide in a Depleted Oil Reservoir", SPE 7256, 2002

² G.N. Breit, "Produced Water Database", United States Geological Survey, 2003.

System performance over
30-minute laboratory-scale run
(synthetic high-TDS San Juan Basin brine)

Sample No.	1	2	3	4	5	6
Collection time (min.)	5	10	15	20	25	30
<i>pH</i>	8.51	8.56	8.49	8.47	8.43	8.44
Precipitation time (sec.)	10	15	11	8	7	9
% change in Ca^{2+}	18.7	16.6	17.7	18.9	19.2	19.8
% change in IC	95	96	96	97	97	97

Identification of precipitates

- X-ray diffraction data confirm that the precipitates formed are calcium carbonate (mostly calcite)
- Scanning electron microscopy reveals calcite with various morphologies, as well as small amounts of needle-like aragonite crystals and plate-like vaterite
- Reduction in IC in solution appears to be associated only with carbonate formation and not with CO₂ outgassing

SEM image of precipitates from synthetic San Juan Basin brine (with BCA)



aragonite

calcite

SEM image of precipitates from synthetic San Juan Basin brine (no BCA)



Sequestration efficiency in single cycle with BCA

mol/l	Permian Basin 45 °C	San Juan Basin Ambient temperature
IC before precipitation	8.1×10^{-3}	7.9×10^{-3}
IC after precipitation	1.0×10^{-3}	0.7×10^{-3}
Efficiency	87%	91%
Ca ²⁺ concentration before precipitation	4.1×10^{-2}	8.4×10^{-2}
Ca ²⁺ concentration after precipitation	3.3×10^{-2}	7.5×10^{-2}
Decrease in Ca ²⁺	20%	11%

Sequestration efficiency in single cycle with BCA

- System performance is stable over 30-minute runs
- Higher Mg^{2+} concentration and $\text{Mg}^{2+}:\text{Ca}^{2+}$ ratio in Permian Basin brine necessitates modest heating to obtain precipitation
- Calcium carbonate precipitation from high-TDS brines is limited by depletion of IC (not cations)
- Can we re-saturate brines with CO_2 and use multiple cycles?

Multiple-cycle tests: 1st cycle (synthetic high-TDS San Juan Basin brine)

Sample No.		1	2	3	4	5	6
Collection time (min.)	Before precipitation	5	10	15	20	25	30
pH	-	8.15	8.46	8.54	8.39	8.47	8.61
Precipitation time (sec.)	-	< 1	< 1	< 1	< 1	10	1
Ca ²⁺ Conc. (mM)	108.1	77.2	77.0	80.8	80.5	84.4	84.1

Multiple-cycle tests: 2nd cycle (synthetic high-TDS San Juan Basin brine)

Sample No.	1	2	3	4	5	6
Collection time (min.)	5	10	15	20	25	30
pH	8.16	8.29	8.23	8.23	8.47	8.20
Precipitation time (sec.)	< 1	< 1	< 1	< 1	< 1	< 1
Ca ²⁺ Conc. (mM)	35.4	40.7	47.9	43.2	48.3	47.6

Multiple-cycle tests: 3rd cycle (synthetic high-TDS San Juan Basin brine)

Sample No.	1	2	3	4	5	6
Collection time (min.)	5	10	15	20	25	30
pH	7.63	7.76	7.86	7.83	7.81	7.75
Precipitation time (sec.)	< 1	< 1	< 1	< 1	< 1	< 1
Ca ²⁺ Conc. (mM)	4.0	11.3	10.5	1.9	10.9	10.2

Multiple-cycle tests: 4th cycle (synthetic high-TDS San Juan Basin brine)

Sample No.	1	2	3	4	5	6
Collection time (min.)	5	10	15	20	25	30
pH	8.02	7.98	8.14	8.12	8.10	8.09
Precipitation time (sec.)	-	-	-	-	-	-
Ca ²⁺ Conc. (mM)	9.3	9.3	9.3	6.9	1.4	1.6

Decrease in Ca^{2+} concentration over four cycles

mM		1 st cycle	2 nd cycle	3 rd cycle	4 th cycle
Ca^{2+} concentration before precipitation	108.1				
Ca^{2+} concentration after precipitation (mean)		80.7	43.9	8.1	6.3
Decrease in Ca^{2+} (%)		25.3	59.4	92.5	94.2

Sequestration potential of Permian and San Juan Basin produced waters

- Results indicate that ~ 93% of Ca^{2+} ions could be used to sequester CO_2 in carbonate form
- Waters produced and reinjected annually in New Mexico and the Permian Basin region of Texas contain ~ 2.07 Mt Ca^{2+} ions

[Based on data from OSE (New Mexico) and Railroad Commission of Texas]

Sequestration potential of Permian and San Juan Basin produced waters

- Produced waters reinjected annually in New Mexico and the Permian Basin region of Texas could be used to sequester ~ 2.14 Mt CO_2 as CaCO_3
- Precipitation of MgCO_3 as well would increase this sequestration potential to ~ 3.26 Mt CO_2 in both carbonates

Acknowledgements

We gratefully acknowledge:

- The support of EPRI through contract numbers WO9000-26 and EP/P11940/C5920
- DOE support through the Southwest Regional Partnership for Carbon Sequestration

References for our earlier work with brines

1. G.M. Bond, N. Liu, A. Abel, B.J. McPherson, and J. Stringer (2004). Biomimetic sequestration of CO₂ in carbonate form: Role of produced waters and other brines. *Prepr. Pap. – Am. Chem. Soc., Div. Fuel Chem.* 49 (1), (227th ACS National Meeting, March 28 – April 1, 2004).
2. G.M. Bond, N. Liu, A. Abel, B. McPherson, and J. Stringer (2004). Laboratory-scale pilot of enzyme-catalyzed CO₂ sequestration with produced waters as cation source. *3rd Annual Carbon Capture and Sequestration Proceedings; ExchangeMonitor Publications 2004; Washington DC; WWWcarbonsq.com.*

3. G.M. Bond, N. Liu, A. Abel, B.J. McPherson and J. Stringer (2004). Early results from a laboratory-scale pilot-plant demonstration of enzyme-catalyzed CO₂ sequestration with produced waters as cation source. Proceedings of the Seventh International Conference on Greenhouse Gas Control Technologies (GHGT-7), (September 5-9, 2004, Vancouver, Canada).
4. N. Liu, G.M. Bond, A. Abel, B.J. McPherson, and J. Stringer (2005). Biomimetic sequestration of CO₂ in carbonate form: Role of produced waters and other brines. *Fuel Processing Technology*, in press.